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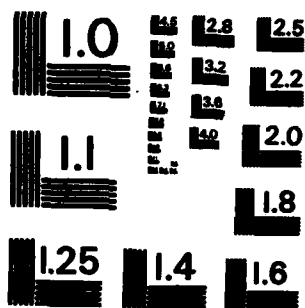
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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHAMPTON

Seventh Periodic and Annual Report

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United States Navy
Office of Naval Research

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Report on Period January 1st 1981 to April 1st 1982

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P. J. Sanders
H. Fleischmann
A. Davick
J. Robinson

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ANNUAL REPORT ON CONTRACT OGD 14 - 77 - 6 - 006

Introduction

The OGE funded research group at Southampton is investigating the molecular identity of the electrode: electrolyte interface using a gradually expanding variety of spectroscopic and related structural/analytical methods. The group can claim with confidence to have pioneered much of the current interest in the use of vibrational spectroscopy (laser Raman and infrared) and X-ray diffraction for this type of investigation. Of the techniques being exploited here, the X-ray diffraction method is the least well developed.

Over the last 1½ years a considerable volume of our work has appeared in the literature, been reported in University of Southampton theses or is in preparation. We give, as the body of this report, a set of Abstracts of most of the papers and theses prepared since January 1981 or in a few cases, a transcript of the introductions to short communications. In the cases where we reference articles or chapters in books containing no abstracts, we give only a reference.

The authors of these papers will be delighted to provide requests or complete copies of the papers[†] on request. To obtain copies please contact the author.

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underlined in the appropriate reference using the addresses:

Department of Chemistry
The University
Southampton SO9 5NH
U.K. or Telex 47001

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P.J. Stedra
10.6.82

We regret that we cannot provide copies of these but it may be possible to arrange inter-library loan facilities. We suggest you investigate this possibility with your own library who should themselves contact the University of Southampton library requesting loan facilities.

Reprints and Chapters published in Books

M. Fleischmann and I.R. Hill: "Electrochemical Effects" in Surface Enhanced Raman Scattering. Eds. S.K. Chang and T.E. Patek, Plenum Press, New York and London (1983) p.275-302.

M. Fleischmann and I.R. Hill 'Raman Spectroscopy' to be published in A Comprehensive Treatise on Electrochemistry, Eds. J. Nechts, S.K. Conway and E. Yeager, Plenum Press, New York and London.

Both of the above contain new information and discussion on the current status of Raman studies at the electrode:electrolyte interface.

A recently prepared chapter

P.J. Hendra, D.J. Cutler and G. Fraser: Laser Raman spectroscopy on Synthetic Polymers, Ch.IV of Developments in Polymer Characterization - 2. Ed. J.V. Suckling, Applied Science Publ. London 1981.

Includes a considerable amount of detailed experimental data on Raman instrument performance characteristics, testing, machine comparisons and performance limits, much of it relevant to this field.



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Review

Appeared in:

Electrochimie und Elektrolyse. Dieemann Monograph.

Vol. 1851 1870

Verlag Chemie 1981.

Structural investigations of electrode-solution interfaces.

Dr. A. Bewick, Professor M. Fleischmann and Dr. J. Robinson,

Chemistry Department, University of Southampton, Southampton SO8 9AH, England.

Three in situ methods for the determination of the structure of the interfacial region between electrodes and electrolyte solutions are discussed: Raman spectroscopy and modulated specular infra red reflectance spectroscopy and transmission X-ray diffraction. It is shown that the structure of the solvent (water) of adsorbed anions in the double layer and of organic adsorbates can be simultaneously determined by Raman spectroscopy; infra red spectroscopy gives detailed information on the clustering of solvent molecules and of chemisorbed species. Whereas the spectroscopies give information on the molecular structure and environment in situ X-ray diffraction gives details about longer range ordering.

Drei in situ Methoden zur Strukturbestimmung des interfacialen Bereichs zwischen Elektrode und Elektrolytlösung werden diskutiert: Raman-Spektroskopie, modulierte IR-Spiegelreflektionspektroskopie und Transmissions-Röntgenbeugung. Es wird gezeigt, daß die Struktur des Lösungsmittels, der adsorbierten Anionen in der Doppelschicht und der adsorbierten organischen Stoffe mittels der Raman-Spektroskopie bestimmt werden kann; die IR-Spektroskopie dagegen gibt detaillierte Information über Zusammenballung von Lösungsmittelmolekülen und über chemisorbierte Stoffe. Während die spektroskopischen Methoden Informationen über die Molekülstruktur und Umgebung geben, erhält man durch die in situ Röntgenbeugung Details über die Ordnung der adsorbierten Schichten.

Trois méthodes in situ pour la détermination de la structure de la région interfaciale entre électrodes et solution électrolytique sont discutées: spectroscopie Raman; spectroscopie infra rouge du pouvoir réflecteur modulé; diffraction rayons-X. Il est montré que la structure du solvant (eau), des anions adsorbés dans la double couche, et des espèces organiques adsorbées peut être simultanément déterminée par spectroscopie Raman. La spectroscopie infra-rouge donne des informations détaillées sur les agrégats de molécules de solvant et sur les espèces chimisorbées. Alors que les spectroscopies Raman et infra-rouge donnent des renseignements sur la structure moléculaire et l'environnement in situ, la diffraction rayons-X donne des détails sur l'arrangement ordonné de l'ensemble des adsorbés.

Alamethicin Induced Conductances in Lipid Bilayers.

II. Decomposition of the observed (compound) process.

Fleischmann, H., Gabrielli C., Labram, H.T.G., Markwart, T.

Department of Chemistry, The University, Southampton SO8 9H1

Abstract

The formalism required for deriving probabilities of the states of a single (elementary) pore, formed by the action of the polypeptide alamethicin in a lipid bilayer membrane, from the observed states of a single (elementary) pore from the observed probabilities of the compound states of the ensemble of pores is developed. Although the analysis has been developed in the context of the evaluation of the statistical properties of pore formation in lipid bilayers, alamethicin being the pore former, the treatment is in fact generally applicable to all situations where the modelling is most readily cast in terms of the behaviour of a single elementary system whilst the experiment deals with ensembles of such systems.

The application of the formalism for the steady state is illustrated in the accompanying paper; empirical extensions to the case of non-steady state are also illustrated.

Alamethicin Induced Conductances in Lipid Bilayers

III. Derivation of the properties of the elementary
processes from the (compound) observed process.

Fleischmann, M., Gabrielli, C., and Lehren, M.T.S.

Department of Chemistry, The University, Southampton.

Abstract

The formalism for the derivation of the probabilities of the states of a single (elementary) pore from the observed probabilities of the compound states of the ensemble of pores, developed in the preceding paper, is extended to cover the transition probabilities between states of the elementary pore. These procedures have been applied to the voltage controlled pore formation in lipid bilayers under the action of alamethicin. Shift in this system is shown to be due to the dependence of the trigger rate for pore creation/destruction on age. The properties of the elementary processes are independent of age; the elementary process exhibits an upper reflecting state (in a statistical sense).

The analysis of fluctuations in the rates of
electrocrystallisation of silver.

Part II Comparison of experimental data at
low overpotentials with models.

E. Budevski, M. Fleischmann, C. Gabrielli and N. Labram

Department of Chemistry, The University, Southampton SO9 5NH

Abstract

It is shown that in the electrocrystallisation of silver on perfect single crystal faces the moments of the transients alone due to crystal growth at low overpotentials (where each layer grows following the formation of a single nucleus) can be interpreted as being due to the two-dimensional growth of circular centres with a uniform probability of nucleation over the substrate surface; the rate determining step of crystal growth takes place at the edges of the circular centres. Nucleation in a stationary state is adequately described as a Poisson process; the nucleation rate may be derived from the amplitude of the "white noise" at low frequencies while the turn over frequency at higher frequencies gives a measure of the mean life time of each transient. The analysis of examples of such experiments however shows that nucleation in the initial stages is more complicated than a simple Poisson process.

The analysis of fluctuations in the rates of electro-
crystallisation of silver. Part I: Experimental Data

E. Budevski, V. Bostanov, M. Fleischmann, C. Gabrielli

M. Labram and W. Obretenov.

Department of Chemistry, The University, Southampton SO9 5NH

Abstract

Experimental data are presented for the electro-crystallisation of silver on perfect single crystal substrates. At low overpotentials (where each layer grows following the formation of a single nucleus) the first four moments of the transients alone are evaluated (moments higher than the first moments expressed as moments about the mean); the statistical properties of ensembles of whole experiments are presented as plots of standard deviation divided by the mean; deposition in a stationary state is characterised by the power spectral density of the deposition process. The statistical properties for deposition at higher overpotentials (where each layer grows via the formation of a large number of nuclei) is characterised by plots of the standard deviation against the time as well as by plots of the standard deviation divided by the mean current against time and $(\text{time})^{-1/2}$. All these methods of evaluation show that much new information about the mechanism of electro-crystallisation is accessible by appropriate modelling of the processes.

Electrocrystallisation

M.Y. Akyash, N. Fleischmann and H. Labrecq

Department of Chemistry, The University,

Southampton SO9 5NH

Abstract

Generalized models of electrocrystallisation under potentiostatic conditions are developed and the current-time transients for special models applicable to the electrodeposition of nickel are derived and tested. It is shown that computer aided fitting procedures allow detailed analyses of the deposition processes to be made and that new kinetic information can be derived. The analysis of the statistics of ensembles of transients and of fluctuations in the stationary state is illustrated by the nucleation and growth of two-dimensional centres of silver and is shown to reveal additional information about electrocrystallisation.

The analysis of fluctuations in the rates of electro-
crystallisation of silver. Part III: Comparison of
experimental data at high overpotentials with models

E. Budevski, M. Fleischmann, C. Gabrielli and M. Lebram

Department of Chemistry, The University, Southampton OS9 5NH

Abstract

Transients for the electrocrystallisation of silver on perfect single crystal faces are interpreted for experiments at high overpotentials (where each layer grows following the formation of a large number of nuclei). An exact model is developed for the formation of the first layer based on the growth of circular centres, growth being limited by overlap; the slow stage of the reaction is assumed to be crystal growth at the edges of the circular centres. It is shown that analysis according to this exact model agrees closely with a more approximate treatment and the latter treatment is extended to cover the formation of the second and third layers. Observation of maxima and minima in plots of the standard deviation divided by the mean current against time are shown to be due to the retardation of nucleation in succeeding layers by the growth of the underlying deposit. It is shown that the statistical analysis leads to the determination of the rate of nucleation separately from the rate of crystal growth as in the case of deposition at low overpotentials. The data show that the rate of nucleation increases markedly at long times although the overall rate of the reaction remains constant.

To be submitted shortly.

Theses - Univ. of Southampton

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Doctor of Philosophy

AN INVESTIGATION OF ELECTRODEPOSITION AND ELECTROCATALYSIS
USING CARBON FIBRE MICROELECTRODES

by Martin William Bayes

Electrodeposition and electrocatalytic processes of ruthenium on carbon fibre microelectrodes (radius 4×10^{-4} cm, area 5×10^{-7} cm²) have been investigated. The use of such small electrodes leads to increased variability in the behaviour of metal deposition transients. This variability, amongst ensembles of transients obtained under identical experimental conditions can be modelled to allow access to kinetic information not directly available from conventional treatment of data from single transients or averaged results.

The majority of the results reported are for the deposition of ruthenium from the solution of its trichloride in aqueous hydrochloric acid, and concomitant hydrogen evolution.

Potentiostatic growth transients for a range of deposition potentials and metal ion concentrations are interpreted in terms of a model invoking Poissonian behaviour of 2-D and 3-D nucleative processes, followed by deterministic metal growth and hydrogen evolution.

Brief examples of the behaviour of other deposition systems are also reported, together with the results of an investigation, carried out in the laboratory of the project's co-sponsors, into the electrochemistry of titanium in aqueous, acidic, fluoride solutions.

Supervisor: Prof. M. Fleischmann.

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Master of Philosophy

AN ELECTROCHEMICAL AND RAMAN SPECTROSCOPIC
STUDY OF SILVER AND PALLADIUM ELECTRODES

by Pierre Robert Graves

Simultaneous surface Raman spectroscopy and differential capacitance measurements of a roughened silver microelectrode in potassium chloride/pyridine solution (0.1M/0.1M) have been employed to study the chemical and structural nature of the electrochemical double layer. It has been shown that high intensity laser excitation samples species normally present on the electrode surface. When electrochemical roughening is performed in the presence of low power laser radiation, a Lewis acid co-ordinated pyridine species is detected by both techniques. This species is irreversibly desorbed at $-0.2V$ (vs SCE). Correlation of capacitance and spectral data suggests that pyridine reorientates in the double layer at $-0.31V$ and -0.44 (vs SCE).

Initial experiments, reported in this thesis, show that surface enhanced Raman scattering is observed from pyridine, coadsorbed with carbon monoxide, on a hydrogen-saturated palladium electrode in potassium chloride solution (0.1M).

Supervisor: Prof. N. Fleischmann

X-ray Diffraction from adsorbed Iodine on Graphite

by

M. Fleischmann, P.J. Hendra and J. Robinson,

Department of Chemistry, The University, Southampton SO9 5NH
England.

Our knowledge of surface structure at the solid/vacuum interface has been acquired largely through the application of high vacuum analytical techniques. Unfortunately these may not be applied in situ to solid/liquid or solid/high pressure gas interfaces which are of greater practical importance. Ex situ investigations have been made but it is probable that the transfers involved result in surface restructuring. It is therefore apparent that in situ techniques are required. Raman spectroscopy¹ is applicable but lacks versatility, whilst neutron diffraction² and SEXAFS³ are promising but depend upon a reactor and synchrotron respectively. X-ray diffraction on the other hand is routinely performed and the theory is well developed though to date it has been assumed to be insensitive to surfaces. We report here the first observation of X-ray diffraction from a 2-D adsorbate, I₂ on carbon, through the use of position sensitive detection to enhance sensitivity.

Surface Enhanced Raman Spectroscopy of $^{12}\text{CN}^-$
and $^{13}\text{CN}^-$ Adsorbed at Silver Electrodes

M. Fleischmann, I.R. Hill and M.E. Pemble*

Department of Chemistry, The University,

Southampton SO9 5NH

*Department of Chemistry, University of

California, Irvine, California 92717, USA.

Abstract

Measurements are reported of the surface enhanced Raman spectra of $^{12}\text{CN}^-$ and $^{13}\text{CN}^-$ (and of isotopically labelled mixtures) adsorbed at silver electrodes. The spectra are shown to arise from a complex species whose coordination number does not change with electrode potential. This species is probably a $[\text{Ag}(\text{CN})_2]^-$ entity having C_{2v} symmetry; at very negative potentials a reduced form of this complex $[\text{Ag}(\text{CN})_2]^{2-}$ coexists with the formally Ag^I species at the surface. The shifts in band position are interpreted in terms of changes in the bond character of the adsorbed CN^- species. The spectrum of water coadsorbed with CN^- is also markedly dependent on the charge density of the adsorbed CN^- groups.

Accepted for publication by J. Electroanal. Chem.

Infra Red Spectroscopy of the Electrode-Electrolyte Interphase

A. Bewick, K. Hummston and B.S. Pons. Electrochimica Acta 25 (1980) 405.

Results from first experiments using in situ electrochemically modulated IR reflectance spectroscopy are described. The method enables vibrational spectra from monolayer amounts of adsorbed species to be obtained even using aqueous electrolytes. Results are discussed from adsorbed hydrogen on Pt in 1M H₂SO₄, from indole adsorbed on a Pt electrode and from water clusters formed on a Pt surface in 1M H₂SO₄.

Infra Red Spectroscopy of the Electrode-Electrolyte Interphase

A. Bewick and K. Hummston, Surf. Sci., 101 (1980) 131

A simple specular reflectance method is described for obtaining the infra red spectra of species in the electrode/electrolyte solution interphase. The method is shown to be sufficiently sensitive to enable aqueous electrolytes to be used. Results are presented indicating the existence of discrete water structures, resembling small clusters of water molecules, in the inner region of the double layer at platinum and electrodes. Preliminary data are also given for adsorbed hydrogen on a platinum electrode.

IR Vibrational Spectroscopy of Species in the Electrode-Electrolyte Solution Interphase

A. Bewick, K. Hummston, J. Robinson and J.W. Russell

J. Electroanal. Chem., 119 (1981) 175

Hydrogen adsorbed on a Pt cathode from 1M H₂SO₄ was investigated using modulated specular reflectance spectroscopy in the uv/visible and in the IR spectral regions. The optical and spectroscopic properties of weakly and strongly bound hydrogen were shown to be strikingly different. Weakly bound hydrogen behaves like a layer of hydrogen atoms covalently bonded to the platinum; $1/R \, dR/d\theta$ is negative over a wide range of wavelength and at an angle of incidence of 45° $(1/R \, dR/d\theta)_p \approx 2(1/R \, dR/d\theta)_s$. A sharp vibrational absorption band is observed at 1.65 μ m and this band appears when weakly bound hydrogen is formed. The band is ascribed to the $(\nu_2 \cdot \nu_1)$ combination band of water attached by hydrogen bonding to the adsorbed hydrogen. On the other hand, strongly bound hydrogen gives positive values of $1/R \, dR/d\theta$ corresponding to a large increase in free electron density in the surface and showing that it differs from weakly bound hydrogen in the nature of its bonding to the surface.

Electroreduction of Methanol on a Pt-Electrode - IR Spectroscopic Evidence for Adsorbed CO species

B. Beden, A. Bewick, K. Hummelen and C. Lamy.

J. Electroanal. Chem. 121 (1981) 343

In situ electrochemically modulated IR spectroscopy is used to identify the adsorbed intermediates formed during electroreduction of methanol at a Pt electrode in aqueous sulphuric acid. Vibrational spectra from two different (CO)_{ads} species were observed: a strong band at about 2070 cm⁻¹ corresponding to a linearly bonded CO species and a weaker band at about 1850 cm⁻¹ corresponding to a bridge bonded CO species. The position of the former band is strongly potential dependent, being at higher energy at more positive values of the electrode potential, and thus the observed band has a bipolar shape in these modulation experiments. No spectroscopic evidence for (COH)_{ads} was obtained.

Structural investigation by infra red spectroscopy of adsorbed hydrogen on platinum

A. Bewick and J.W. Russell. J. Electroanal. Chem. 132 (1982) 329

The formation of weakly bound hydrogen on a polycrystalline platinum electrode was found to be associated with the appearance of a number of IR absorption bands in the range 1.6 μm to 7.5 μm. Spectra from aqueous acid electrolytes, fully deuterated systems and mixed H₂O / D₂O systems were analysed. The band assignments and their relative intensities lead to a model for weakly bound hydrogen in which the hydrogen atom is bonded to a particular water structure. The enhanced intensities of combination bands are ascribed to the effect of the intense electrical field in the electrical double layer.

Structural investigation by electrochemically modulated infra red spectroscopy of adsorbed hydrogen on rhodium

A. Bewick and J.W. Russell.

J. Electroanal. Chem. (accepted for publication)

Measurements were made, in situ, by IR reflectance spectroscopy at a rhodium electrode in H₂SO₄ and mixed H₂SO₄/D₂SO₄ electrolytes to give spectra corresponding to the difference between the state of the electrode at a potential in the double layer region and at a potential in the hydrogen adsorption region. A model for weakly adsorbed hydrogen in which the adsorbed atom is bonded to an oriented water structure is discussed from the spectral data. The spectra also show the presence of a strongly bound hydrogen species although the corresponding bands are obscured by the intense electrical field.

Published in: *J. Electroanal. Chem.* 117 (1981)

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AN ELECTROCHEMICAL STUDY OF THE ADSORPTION OF PYRIDINE AND CHLORIDE IONS ON SMOOTH AND ROUGHENED SILVER SURFACES

M. FLEISCHMANN, J. ROBINSON and E. WAGER*

Chemistry Department, University of Southampton, Southampton SO9 5NH (England)

(Received 20th May 1980)

INTRODUCTION

The potential dependence of the double-layer capacitance of single-crystal and polycrystalline silver electrodes in the absence of specific adsorption (sodium fluoride and sodium sulphate electrolytes) has been extensively investigated in recent years [1,2] (and references quoted therein). There have also been a number of double-layer studies of the specific adsorption of halide ions on single-crystal [3] (and references quoted therein) and polycrystalline electrodes [4] while the adsorption of pyridine has been investigated by spectrophotometry [5] and by a radio tracer method [6].

On the other hand, there have been extensive investigations of the Raman spectra of pyridine adsorbed on silver electrodes in the presence of chloride ions (for reviews covering a substantial part of this field, see refs. 7 and 8); the major effort in the Raman spectroscopy of electrode-solution interfaces has been devoted to this system). It has been well established that the Raman-scattering cross-section of the adsorbed species is many orders of magnitude higher than that of the species in solution [9,10] provided measurements are performed by at least one counter-electrode polarization sequence to roughen the electrodes; then roughening procedures have been used for both single-crystal and polycrystalline silver electrodes.

The major aim of most of the Raman spectroscopic studies has been to find the cause of the enhanced Raman scattering, and there has been little attempt so far to relate the measurements to the electrochemical behaviour of the system. The main objective of the work reported in this paper has been the definition of the characteristics of the double-layer capacitance of smooth and roughened single-crystal and polycrystalline silver electrodes in sodium fluoride electrolytes containing chloride or pyridine ions, as well as pyridine in the presence of chloride ions and to relate these characteristics to the Raman spectra.

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